

*Jackson (H. L.)*



XII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS. ✓

By C. LORING JACKSON.

TENTH PAPER.

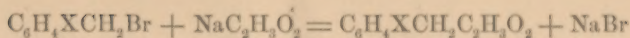
THE RELATIVE CHEMICAL ACTIVITY OF CERTAIN SUBSTITUTED BENZYL BROMIDES.

Presented November 12, 1879.

IN the following paper I have the honor of laying before the Academy an account of some experiments undertaken to compare the ease with which bromine can be removed from the side-chains of the substituted benzylbromides described in the first paper of this series; in other words, an attempt to establish some relation between the structure of a molecule and its chemical activity. The differences in structure, which I have taken up, are of two sorts, — those depending on difference in the position of the same element, as in the three monobrombenzylbromides; and those depending on the presence of different but related elements in the same position, as in parachlor-, parabrom-, and paraiodbenzylbromide.

After a careful consideration of the reagents by which the side-chain bromine could be removed from these substances in a simple metathetical reaction, I decided that sodic acetate promised the best results, and, after many experiments, adopted a method, which consisted in treating equivalent amounts of the substituted benzylbromides, for the same length of time and under the same conditions, with an alcoholic solution of sodic acetate, and determining by volumetric analysis the amount of sodic bromide formed from each according to the following general reaction, —

*box 158*



in which X stands for the halogen atom attached to the benzol ring. But even this reaction, although less full of sources of error than most of those available, is not so well adapted to work of this sort as I could wish; since the action takes place so rapidly that small differences in the time of two experiments produce comparatively large differences in their results. I have tried, therefore, to make the time occupied in starting and stopping the action as short as possible, and have reduced the duration of the addition of the sodic acetate solution, by which the reaction is started, to five seconds; but I have not been so successful in stopping the reaction promptly, as this was done by precipitating the organic matter with water, of which so large a quantity was needed that the average duration of the addition was fifteen seconds.

This method of stopping the reaction by means of water is not above criticism; for, although I consider of little or no weight the possible objection that the reaction may continue forming more sodic bromide after the addition of water, yet the presence of even a small amount of the substituted benzylbromide will cause a serious error in the determination of the sodic bromide,\* and it is very hard to remove this completely by filtration; that it is possible, however, if sufficient care is used, appears from the following experiment:—

A mixture of parabrombenzylbromide and parabrombenzylacetate was dissolved in a little alcohol, and, after precipitating with water and filtering, 4 c.c. of a standard solution of argentic nitrate added, upon titrating the liquid 5.3 c.c. of the standard solution of potassic sulphocyanate were found to be necessary, the theoretical quantity being 5.27 c.c.

In selecting a solvent, it was necessary to find one which would dissolve all the substances entering into the reaction; since Berthelot and Pean de St. Gilles† have shown that, when two liquids which do not mix are used, the amount of action depends to a large extent on the

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\* This point is illustrated by the following experiments: A little parabrombenzylbromide was dissolved in alcohol, and precipitated with water; 2.30 c.c. of a standard solution of argentic nitrate were added, and the mixture allowed to stand fifteen minutes; on titrating for silver, it was found that 0.41 c.c., corresponding to 0.0069 gm. of  $\text{AgNO}_3$ , had been lost, while another similar sample which stood for one hour and twenty minutes lost 1.59 c.c., corresponding to 0.026 gm. of  $\text{AgNO}_3$ .

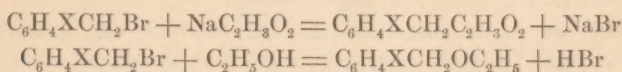
† Ann. Chim. Phys., 3d ser., lxvi. p. 46; lxviii. p. 238.



size of the surface of contact; and therefore no constant results can be expected. I have confirmed these observations, while studying the action of water on the substituted benzylbromides, as will be described later in this paper. Under these circumstances, alcohol seemed to be the only solvent admissible; but its use introduced a new source of error, since it acts on the benzylbromides, forming the corresponding ethyl ethers and hydrobromic acid, as is shown by the following experiment.

Some parabrombenzylbromide was boiled with absolute alcohol for fifteen minutes. After removing the organic matter by precipitation with water and filtration, a precipitate was formed on the addition of argentic nitrate.

This defect was removed as completely as possible by taking pains that the benzylbromides should be in contact with the alcohol for the same length of time in each series of experiments. Then the results depended, in each case, on two reactions, viz. :—



but, as the time of each was the same in all the experiments of a series, the occurrence of the second did not materially affect the result, especially as the amount of substance entering into this second reaction was very small.

The adjustment of the amount of alcohol to be used was no easy matter, because sodic acetate and bromide are very sparingly soluble in absolute alcohol, and any considerable dilution interferes with the solubility of the benzylbromides; nor could the difficulty be removed by increasing to any great extent the amount of alcohol, as this would have increased the length of time necessary to stop the reaction.

More important than any of the sources of error yet mentioned is that proceeding from the differences in volatility of the benzylbromides with alcohol vapor, since this must alter the amount of substance capable of entering into the reaction in each case by the quantity of bromide volatilized with the alcohol in the upper part of the flask; and it is principally to this cause, which I could find no way of removing, that I am inclined to ascribe the considerable variations in my results.

This discussion of the defects in the process shows that no absolute agreement in the numbers obtained can be expected; but they agree nearly enough to establish certain interesting relations between the rates of decomposition of some of these compounds.

*Comparison of the Three Monobrombenzylbromides.*

One gramme of each substance was weighed in a wide-mouthed flask, the cork of which was fitted with a return-condenser and a short wide tube closed with a cork for the addition of the reagents, 10 c.c. of absolute alcohol were added, and the mixture heated for seven minutes in a boiling water-bath. After which, 25 c.c. of a saturated solution of sodic acetate in 99 per cent alcohol, at  $60^{\circ}$  to  $70^{\circ}$ , were introduced, and the flask heated for a definite time, varied in each series of experiments; care being taken that the water-bath boiled violently during the whole time, and that the three flasks to be compared were immersed to the same depth, and arranged symmetrically in the bath. The action was stopped by the addition of a large quantity of water, the flask being removed from the bath at the same time; and, after filtering out the organic matter, the quantity of sodic bromide formed by the reaction was determined by Volhard's \* excellent method of titration with sulphocyanate.

The brombenzylbromides used were made in the way described in the first paper † of this series, and purified with the utmost care.

The sodic acetate was prepared by drying the crystallized salt in an air-bath. It yielded on analysis the following result:—

0.7720 grm. of  $\text{NaC}_2\text{H}_3\text{O}_2$  gave 0.6655 grm. of  $\text{Na}_2\text{SO}_4$ .

	Calculated.	Found.
Sodium	28.05	27.93

The absolute alcohol did not turn anhydrous cupric sulphate blue, and neither it nor the acidified solution of the sodic acetate gave a precipitate with argentic nitrate.

The 25 c.c. of the alcoholic solution of sodic acetate contained a little more than enough of the salt to decompose the one gramme of brombenzylbromide used, since,—

10 c.c. of this solution yielded on evaporation 0.136 grm. of sodic acetate, and therefore,—

25 c.c. contained . . . . .	0.340 grm.
Needed for 1 grm. brombenzylbromide . . .	0.328 grm.
Excess . . . . .	0.012 grm.

\* Ann. Chem. u. Pharm., exc. p. 1.

† These Proceedings, vol. xii. (N. S. iv.) p. 211.

The 35 cc. of alcohol present were much more than sufficient to dissolve all the sodic bromide formed, as a rough determination showed that, —

35 c.c. of absolute alcohol dissolve 0.627 gm. NaBr.

1 gm. brombenzylbromide yields 0.412 gm. NaBr.

All the substances, therefore, were in solution throughout the experiment.

The accuracy of the method was tested by the following experiments, in each of which two portions of parabrombenzylbromide were compared : —

I. Time, five minutes.

A.	1 gramme parabrombenzylbromide lost	0.1164 gm. Br.
B.	“ “ “	0.1102 gm. Br.
Difference . . . . .		0.0062 gm. Br.

	Percentage of total side-chain bromine removed.	B in per cent of A.
A.	36.39	100.0
B.	34.47	94.7
	1.92	5.3

II. Time, seven minutes.

A.	1 gm. parabrombenzylbromide lost	0.1484 gm. Br.
B.	“ “ “	0.1446 gm. Br.
Difference . . . . .		0.0038 gm. Br.

	Percentage of total side-chain bromine removed.	B in per cent of A.
A.	46.36	100.
B.	45.21	97.5
	1.15	2.5

From these results it appears that the method can be trusted within 0.0062 gm. of bromine, or 5.3 per cent when the largest number is taken as 100.\*

The results of the experiments, comparing the rate of decomposition of the three monobrombenzylbromides, are given in the following table; the first column of which gives the time from the addition of

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\* The results of these experiments cannot be compared with those given in Table I., because the quantity of alcohol used was not the same.



the acetate till the reaction was stopped by dilution with water, while, in the other columns, under the name of each substance the amount of bromine removed is given, — first in grammes, and second in percentages of the total amount of side-chain bromine.

TABLE I.

Time in minutes.	Parabrombenzylbromide.		Metabrombenzylbromide.		Orthobrombenzylbromide.	
	Bromine in grammes.	Per cent of total.	Bromine in grammes.	Per cent of total.	Bromine in grammes.	Per cent of total.
5	0.0855	26.73	0.0621	19.41	0.0533	16.65
10	0.1261	39.41	0.0968	30.25	0.0700	21.88
20	0.1762	54.75	0.1329	41.54	0.1015	31.72
30	0.1880	58.76	0.1517	47.43	0.1412	44.13

On representing the percentages of the total side-chain bromine removed by curves, in which horizontal distance represents time, vertical per cents, it is found that those given by the para and meta compounds are comparatively regular, but that the ortho curve is decidedly irregular. The same fact is brought out by the following table, in which the amount of bromine removed from the ortho and meta compounds in each experiment is given in percentages of the amount derived from the para compound in the same experiment.

TABLE II.

Time in minutes.	Para.	Meta.	Ortho
5	100	73.	62.
10	100	77.	55.
20	100	76.	58.
30	100	81.	75.

The differences between the relative amounts of bromine removed from the meta compound in the first three experiments, tabulated above, fall within the limit of error of the process, which amounts to over five per cent when the numbers are given in this form; and, although the amount of bromine removed during thirty minutes is somewhat larger, the difference between this and the highest of the other numbers is only four per cent. It is probable, therefore, that the relative rate of decomposition for the para and meta compounds remains constant in the interval of time between five and thirty minutes; and that the slight increase in the numbers with the time in the experiments at 5, 20, and 30 minutes, is entirely accidental, although

this point can be settled only by a new series of observations with a more accurate method. If this is assumed to be true, the mean of the numbers given in the meta column will represent the rate at which the metabrombenzylbromide is attacked, in comparison with that for the para compound taken as 100. This mean is 77; that is, about three quarters as much bromine is removed from the meta as from the para compound in the same length of time.

The numbers given in the ortho column show much more serious deviations, the maximum difference amounting to twenty per cent; but, as I observed that these numbers increased essentially with the time during which the specimen had stood exposed to the air of a desiccator, the experiments having been tried in the following order,—10 minutes, 55 %; 5 minutes, 64 %; 20 minutes, 58 %; 30 minutes, 75 %,—I was led to the conclusion that the substance was undergoing decomposition, which afterwards was proved to be the case by the following analyses: I. made before, II. and III. after, the series of experiments.

- I. 0.2375 grm. of orthobrombenzylbromide gave, by the method of Carius, 0.3565 grm. AgBr.
- II. 0.2950 grm. of substance gave 0.3705 grm. AgBr.
- III. 0.4100 grm. of substance gave 0.5210 grm. AgBr.

Calculated for $C_7H_5Br_2$ .		Found.		
		I.	II.	III.
Bromine	64.00	63.87	53.46	54.07 *

The complete study of this decomposition must be postponed till a future paper. I can only say here, that no appreciable amount of free hydrobromic acid could be detected in the substance analyzed above, and that I have often found crystals of orthobrombenzoic acid in specimens of orthobrombenzylbromide which had stood exposed to dry air for several months. Whatever may be the nature of the change, it is evident that the ortho numbers are of no value; and no attempt was made to correct them by new experiments, because such an unstable substance as the orthobrombenzylbromide is entirely unfit for work of this sort.

I will add a number of other comparisons, which were made by less accurate processes during the elaboration of the method. They are given as in Table II., the amount of bromine removed from the para

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\* As these experiments were made before the orthobrombenzylbromide was obtained in the solid state, I had no criterion of its purity except the analysis.

compound being taken as 100 in each experiment, and the amounts from the meta and ortho compounds given in percentages of this. Either two or four grammes of substance were taken in each experiment.

TABLE III.

Time in Minutes.	Para.	Meta.	Ortho.
22	100	78	54
22	100	73	52
23	100	78	54
21	100	—	48
Mean,	100	76	52

These numbers, entitled to very little consideration as independent experiments, confirm the preceding results from the meta compound, even more closely than could be expected when the large limit of error is remembered; and further would seem to indicate that the rate for the ortho compound is about one half that for the para, if it is assumed, as before, that the relative rate does not vary with the length of time during which the reaction has run; a result confirmed by the experiment made first in the preceding series, and therefore entitled to the most weight, which gave 55 %.

Berthelot and Pean de St. Gilles,\* in their classic researches on etherification, found that after a certain time the water set free in the reaction prevented further formation of the ether; in other words, that there was a limit to etherification. Although it did not seem probable that there would be such a limit to this reaction, some experiments were tried to test the question, with the following results:—

I. Time somewhat more than two hours:—

1 grm. of parabrombenzylbromide lost 0.3203 grm. of bromine.

1 grm. of metabrombenzylbromide lost 0.2701 grm. of bromine.

0.8200 grm. of parachlorbenzylbromide lost 0.3082 grm. of bromine.

To this may be added the following, in which the method was somewhat different; in II. common alcohol being used, and in III. the reaction taking place in a sealed tube, with dilute alcohol as the solvent.

II. Two portions of parabrombenzylbromide, 1 grm. each, lost in twenty-five minutes 0.3113 grm. and 0.3074 grm. of bromine.

III. In thirty minutes 0.3046 grm. and 0.3093 grm. of bromine.

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\* Ann. Chim. Phys., 3d ser., lxxviii. p. 225.



The results of these three experiments, calculated into percentages of the side-chain bromine, are given for the sake of comparison in the following table:—

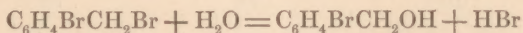
TABLE IV.

I.	II.	III.
Para. 100.1	Para. 97.3	Para. 95.3
Meta. 84.4	“ 96.1	“ 96.7
Chlor. 96.4		

Owing to the different conditions under which they were made these series of experiments are not comparable with each other, or with the series given in Tables I. and II., even I. not having been made under exactly the same conditions; they show, however, that there is no limit to the reaction in the case of the parabrombenzylbromide and probably none in the case of any of these substances.

*Action of Water on the Monobrombenzylbromides.*

Another entirely different method was also tried, which consisted in heating the substituted benzylbromides with water in sealed tubes, and determining the amount of hydrobromic acid formed by the reaction,—



For this purpose one gramme of each substance was weighed in a tube about 14 cm. long and 2 cm. wide; 5 c.c. of water were added, and, after sealing, the tubes were put into a hot chloride of calcium bath, provided with an air-tight tin cover carrying a return-cooler, which thus was kept at a constant temperature throughout the process. After a definite time the tubes were removed, cooled as rapidly as possible with cold water, and the contents washed into a beaker, and titrated with a standard solution of baric hydrate. The following experiments were made with two portions of parabrombenzylbromide to test the process.

	Time in Hours.	Temperature.	Percentage of side-chain bromine removed.	
			Portion a.	Portion b.
I.	2	132°–134°	16.05	13.3
II.	2½	110°–134°	17.8	16.3
		I.	II.	
	a	100	100	
	b	83	92	

The marked want of agreement between these numbers is undoubtedly due to the fact that the mixture was not homogeneous, and therefore the differences in size of the surface of contact between the water and benzylbromide in the different tubes had a marked effect on the result [Compare p. 242].

In spite of the inaccuracy of the method two experiments were carried through with the following results:—

TABLE V.  
TEMPERATURE 135°.

Time in hours.	Parabrombenzylbromide.		Metabrombenzylbromide.		Orthobrombenzylbromide.	
	Bromine in grammes.	Per cent of total.	Bromine in grammes.	Per cent of total.	Bromine in grammes.	Per cent of total.
6	0.1421	43.85			0.0763	23.55
6	0.1268	39.15	0.0969	29.9	0.0918	28.35

These results calculated into the form of Table II. become:—

Para.	Meta.	Ortho.
100		54
100	76	72

The very high number for the ortho compound in the second experiment is probably due to a previous decomposition of the substance similar to that observed in the principal series of experiments [See page 247]. The other results, as far as they go, confirm those obtained by the acetate method.

In the following table all the numbers thus far obtained are compared:—

TABLE VI.  
ACETATE METHOD.

Time.	Para.	Meta.	Ortho
5'	100	72	64
10'	100	77	55
20'	100	76	58
30'	100	81	75
21'	100	—	48
22'	100	78	54
22'	100	73	52
23'	100	78	54

WATER METHOD.			
6 hours	100		54
6 hours	100	76	72
Mean	100	76	59

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A series of comparative experiments with parachlorbenzylbromide, parabrombenzylbromide and paraiodbenzylbromide was also made by the sodic acetate method, which indicated that they lose bromine at the same rate, when they are used in molecular proportions. I will give here, however, only the results from the last series of experiments, as in the others I did not succeed in overcoming some of the sources of error mentioned in the introduction wholly to my satisfaction. These results are given as in Table II.

Time in Minutes.	Parachlorbenzylbromide.	Parabrombenzylbromide.	Paraiodbenzylbromide.
25	100	97	99

### Summary.

The results of this investigation are, — 1. The side-chain bromine is removed from the three monobrombenzylbromides approximately at the following rates : —

Para.	Meta.	Ortho.
100	76	55 (?)
or 4	3	2 (?)

when the quantity removed is less than 60 per cent of the whole.

2. From parachlor-, parabrom-, and paraiodbenzylbromide at essentially the same rate, if quantities proportional to their molecular weights are used.

All these results need confirmation by more accurate experiments, but, as Menschutkin in one of the papers\* of his beautiful series on the rate of etherification (the first† of which was published a year after the appearance of a preliminary notice‡ of my work) has announced his intention of studying the effect of aromatic isomerism, and with his better chosen reaction and more delicate method will be able to do the work much more easily and accurately than I could, I have decided not to pursue the subject farther.

So far as I have been able to find, the only paper on this subject, as yet published, is one by Post and Mehrtens,§ who describe a single

\* Ann. Chem. Pharm., 197, p. 225.

† Ber. d. ch. G. 1876, p. 931.

‡ Ber. d. ch. G. 1877, p. 1728.

§ Ber. d. ch. G. 1875, p. 1549.



attempt to make out the relative acidity of the three nitrophenols by treating weighed amounts of baric carbonate with solutions of the corresponding quantity of the three isomeres, and after one week determining the amount of baric carbonate dissolved. In this way they got results which calculated in percentages of the amount from the para compound become:—

Para. m.pt. 115°.	Meta. m.pt. 96°.	Ortho. m.pt. 45°.
100	57	93

and, therefore, agree with mine neither in order nor ratio.

### ELEVENTH PAPER.

As the preceding paper has brought the first part of these researches to a conclusion, I have thought it best to give in the present paper certain corrections and additions which will leave this division of the subject in a more satisfactory state.

#### *Parabrombenzyl Compounds.*

In preparing the alcohol of this series during the work described in the preceding paper, I was surprised to find that its melting-point was much higher than that given by Mr. Lowery in the second paper\* of the series, and as in addition to this some portions of that work were left in a decidedly fragmentary state, I have thought it best to submit the parabrombenzyl compounds to a complete revision, which I have done with the following results:—

*Parabrombenzylalcohol*,  $C_7H_7BrCH_2OH$ . This was prepared from the acetate, and purified by crystallization from ligroin, which is by far the best solvent for all the derivatives of the substituted benzyl-bromides described in these papers.

0.2298 grm. of substance gave 0.3765 grm. of  $CO_2$  and 0.0789 grm. of  $H_2O$ .

Calculated for $C_7H_7BrOH$ .		Found.
Carbon	44.92	44.69
Hydrogen	3.74	3.82

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\* These Proceedings, xii. (n. s. iv.) p. 221.

The melting-point of the pure alcohol was  $77^{\circ}$ .\* In other respects its properties are given correctly by Mr. Lowery.

*Parabrombenzylcyanide* melts at  $47^{\circ}$  ( $46^{\circ}$  Lowery). The *alpha-toluylic acid* as before at  $114^{\circ}$ .

*Parabrombenzylsulphocyanate*,  $C_6H_4BrCH_2SCN$ , melts at  $25^{\circ}$  as given by Mr. Lowery. As this melting-point is much lower than would be expected from that of the benzylsulphocyanate ( $36^{\circ}$ – $38^{\circ}$  Henry,  $41^{\circ}$  Barbaglia), I thought it advisable to confirm its formula by the following new analyses:—

0.2318 grm. of substance gave 0.2447 grm. of  $BaSO_4$ .

0.3804 grm. of substance gave 0.3125 grm. of  $AgBr$ .

	Calculated for $C_7H_6BrSCN$ .	Found.
Sulphur	14.03	14.50
Bromine	35.09	34.95

*Parabrombenzylamines*. Parabrombenzylbromide acts on alcoholic ammonia in the cold, giving a mixture of the three amines, or their bromides, from which the pure compounds can be easily obtained by washing out the bromide of the primary amine with water, treating the residue with sodic hydrate, and separating the secondary from the tertiary by crystallization from alcohol.

The *primary amine*, set free from its bromide with sodic hydrate, is an oil, which can be distilled with steam, and is soluble in ether; it is rapidly converted into the carbonate by exposure to the air.

The *carbonate*, obtained by treating the free base with carbonic dioxide, consists of little white prisms arranged in radiating groups, which melt at  $131^{\circ}$ – $133^{\circ}$ , are soluble in water and alcohol, insoluble or nearly so in ether, benzol, and carbonic disulphide.

The *chloride*, made from the carbonate with hydrochloric acid, forms flattened needles melting with apparent decomposition at  $260^{\circ}$ , soluble in water and hot alcohol, but slightly soluble in cold alcohol, and essentially insoluble in ether, benzol, and carbonic disulphide.

The *chlorplatinate*  $(C_6H_4BrCH_2NH_2)_2 PtCl_6$  made from the chloride, and purified by washing with water, gave the following result on analysis:—

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\* The high melting-point of the parabrombenzylalcohol made me think that the paraiodbenzylalcohol might melt at a temperature higher than that given by Mr. Mabery in the third paper of this series. He has, however, at my request recrystallized some of it from ligroin, and found that the melting-point remained the same ( $72^{\circ}$ ) even after three crystallizations.

0.3020 grm. of the salt gave 0.0755 grm. of Pt.

Calculated for $(C_6H_4BrNH_2)_2 \cdot PtCl_6$ .	Found.
Platinum 25.16	25.00

It crystallizes in orange-brown plates, apparently of the monoclinic system, grouped in forms like frost, and is but slightly soluble in cold water, more so in hot, and in alcohol.

The *secondary amine*  $(C_6H_4BrCH_2)_2NH$  is left on evaporating its alcoholic solution as an oil, which solidifies on stirring, and can be obtained crystallized. It melts at  $50^\circ$ , and is very freely soluble in alcohol and ether.

The *chloride* is obtained in glistening rhombic scales, often pen- nately twinned, by adding strong hydrochloric acid to an alcoholic solution of the base; it melts at  $283^\circ$ , and is nearly insoluble in cold, somewhat more soluble in hot water, or alcohol, insoluble in ether.

The *chlorplatinate*  $[(C_6H_4BrCH_2)_2NH_2]_2PtCl_6$  formed by adding chlorplatonic acid to an alcoholic solution of the free base, after being washed with alcohol, and dried at  $100^\circ$ , gave the following result on analysis:—

0.4716 grm. of salt gave 0.0802 grm. of Pt.

Calculated for $[(C_6H_4Br)_2NH_2]_2PtCl_6$	Found.
Platinum 17.58	17.01

It is a yellow powder, nearly insoluble in alcohol and water.

The *tertiary amine*  $(C_6H_4BrCH_2)_3N$  was purified by recrystalliza- tion from ether, or from ligroin; in either case a matted mass of needles looking like cotton was obtained, but the melting-point differed according to the solvent used, the crystals from ligroin showing the constant melting-point  $92^\circ$ , those from common ether the constant melting-point  $76^\circ$ – $78^\circ$ . Two recrystallizations from ligroin were enough to raise the melting-point of the crystals from ether to  $92^\circ$ , while the same number from ether lowered it again to  $76^\circ$ – $78^\circ$ . The following analyses, however, prove that the substance dried *in vacuo* has the composition of the tertiary amine, whichever solvent was used in its purification.

- I. 0.3800 grm. of the crystals from ligroin, m.pt.  $92^\circ$ , gave 0.6680 grm.  $CO_2$  and 0.1200 grm.  $H_2O$ .
- II. 0.2515 grm. of the crystals from ether gave 0.4430 grm.  $CO_2$  and 0.0890 grm.  $H_2O$ .

0.2020 grm. of the crystals from ether gave 0.2175 grm. AgBr.

0.1888 grm. gave 0.2022 grm. AgBr.



	Calculated for (C <sub>7</sub> H <sub>6</sub> Br) <sub>3</sub> N.	I. (Ligroin.)	Found.	II. (Ether.)
Carbon	48.09	47.93		48.03
Hydrogen	3.44	3.51		3.93
Bromine	45.81		45.82	45.56

*Properties.* Fine white needles matted together into a woolly mass, or forming circular radiated groups, insoluble in water, very slightly soluble in alcohol hot or cold, not freely in warm ether, but easily in hot ligroin, from which it crystallizes on cooling. In the preparation from alcoholic ammonia and parabrombenzylbromide it sometimes appears in needles 12 cm. long.

No definite chloride could be obtained even by precipitating the platinum as sulphide from the chlorplatinic acid, and washing with alcohol, as this gave only a viscous varnish.

*Triparabrombenzylamine Chlorplatinic* [(C<sub>6</sub>H<sub>4</sub>BrCH<sub>2</sub>)<sub>3</sub>NH]<sub>2</sub>PtCl<sub>6</sub> made by adding chlorplatinic acid to an ethereal solution of the free base, and purified by washing with water, alcohol, ether, and ligroin, gave the following result on analysis:—

0.3254 grm. of the salt gave 0.0432 grm. of Pt.

	Calculated for [(C <sub>6</sub> H <sub>4</sub> Br) <sub>3</sub> NH] <sub>2</sub> PtCl <sub>6</sub> .	Found.
Platinum	13.51	13.28

Corn-yellow indistinct crystals, insoluble or nearly so in all the common solvents.

*Monoparaiodbenzylamine, C<sub>6</sub>H<sub>4</sub>ICH<sub>2</sub>NH<sub>2</sub>.*

Mr. C. F. Mabery has, at my request, prepared this substance, which he had not obtained in quantity sufficient for analysis, when he published his paper on the paraiodbenzyl compounds, by heating paraiodbenzylbromide with a large excess of alcoholic ammonia in a sealed tube to 120°. It is easily separated from the secondary and tertiary amines by washing with water, and, upon adding sodic hydrate to the solution of its bromide thus obtained, and extracting with ether, the carbonate is left as the ether evaporates in the form of a white solid melting at 113°.

The *chloride* made from the carbonate with hydrochloric acid forms slender white needles melting at 240°, readily soluble in water and alcohol, sparingly in ether.

The *chlorplatinic* (C<sub>6</sub>H<sub>4</sub>ICH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>PtCl<sub>6</sub> made by adding chlor-

platinic acid to the chloride, and purified by washing with alcohol, gave the following result on analysis:—

0.3560 grm. of the salt gave 0.0795 grm. Pt.

Calculated for $(C_7H_6INH_{3/2})_2PtCl_6$ .		Found.
Platinum	22.47	22.34

### *Metabrombenzyl Compounds.*

In the study of these substances which I undertook with Mr. J. Fleming White, so many difficulties were encountered that the work was far from done at the end of the last college year. As, however, Mr. White has left Cambridge, and I see no immediate prospect of returning to this subject, I have decided to publish our results on the alcohol, and the melting-point of the alphetoluylic acid, reserving an account of the amines until our, at present contradictory, results have been submitted to a thorough revision.

*Metabrombenzylalcohol*,  $C_6H_4BrCH_2OH$ , was made directly from metabrombenzylbromide by heating it with water in a sealed tube to  $130^\circ$  for 24 hours, or from the acetate, obtained by heating the bromide with an alcoholic solution of sodic acetate, by decomposing it with aqueous ammonia in a sealed tube at  $150^\circ$ , or with an aqueous solution of sodic hydrate in a flask with a return-cooler. The oil thus obtained was purified by distillation with steam, dried *in vacuo* and analyzed.

0.2890 grm. of substance gave according to Carius 0.2913 grm. AgBr.  
0.4660 grm. gave 0.4690 grm. AgBr.

Calculated for $C_7H_6BrOH$ .		Found.	
Bromine	42.79	42.88	42.84

The substance is a colorless oil heavier than water, which did not solidify in a freezing mixture even when vigorously stirred with a sharp rod.

The *cyanide*, as obtained by the action of an alcoholic solution of potassic cyanide on metabrombenzylbromide, is a dark-colored oil, and is converted by heating with strong hydrochloric acid in a sealed tube to  $115^\circ$  into the *metabromalphetoluylic acid*, melting-point  $97^\circ$ , which resembles the isomeric acids already described very closely. The complete study of this acid must be postponed for the present.

